ions from [isoxazole]$^{\bullet+}$, [oxazole]$^{\bullet+}$, and [vinylene carbonate]$^{\bullet+}$ have the ketene structure. Thus, ca. 50, 35, and 17%, respectively, of the $[H_2, C_2, O]^{\bullet+}$ ions generated upon dissociative ionization of the three precursors must have the ketene structure. The observed instability of oxirene is in keeping with the absence of *direct* experimental evidence for the role of oxirenes in the Wolff rearrangement; although sought,[3] no oxirenes have been isolated or spectroscopically observed.

The significant $[CH_2{=}C{=}O]^{\bullet+}$ content of the source-generated *m/z* 42 ions from [oxazole]$^{\bullet+}$ is compatible with the presence of only a weak broad component in the metastable peak for their generation in the second field-free region (see above). As found for [vinylene carbonate]$^{\bullet+}$, for *source-generated* $[H_2, C_2, O]^{\bullet+}$ ions the more energy-demanding process, i.e. generation of $[CH_2{=}C{=}O]^{\bullet+}$, becomes relatively more important. This behavior has been observed before. For example,[9] (short-lived) $[ClCH_2COOH]^{\bullet+}$ ions fragmenting in the ion source produce mainly the less stable $[H_3, C, Cl]^{\bullet+}$ isomer, $[H_2CClH]^{\bullet+}$, whereas the metastably fragmenting ions largely yield $[CH_3Cl]^{\bullet+}$.

Conclusions

It has been shown that [vinylene carbonate]$^{\bullet+}$, [oxazole]$^{\bullet+}$, and [isoxazole]$^{\bullet+}$ generate the oxirene radical cation, $[\overline{CH{=}CHO}]^{\bullet+}$. The small differences in the collisional activation mass spectra of the source-generated *m/z* 42 ions from these precursors were explained by the cogeneration of [ketene]$^{\bullet+}$. On the basis of neutralization–reionization experiments, it was established that vinylene carbonate, oxazole, and isoxazole generate ca. 17, 35, and 50%, respectively, of $[CH_2{=}C{=}O]^{\bullet+}$ in addition to $[\overline{CH{=}CHO}]^{\bullet+}$ upon dissociative ionization in the ion source of the mass spectrometer. A more pure flux of $[\overline{CH{=}CHO}]^{\bullet+}$ was obtained upon collision-induced fragmentation of [vinylene carbonate]$^{\bullet+}$ in the first field-free region. From a comparison of the latter CA mass spectrum with that of the corresponding source-generated $[H_2, C_2, O]^{\bullet+}$ ions, which contain only 17% $[CH_2{=}C{=}O]^{\bullet+}$, it can be concluded that the former spectrum will be close to that for pure [oxirene]$^{\bullet+}$.

The neutralization–reionization mass spectra of the source-generated *m/z* 42 ions from the three precursors are dominated by *m/z* 28, $[CO]^{\bullet+}$, and *m/z* 14, $[CH_2]^{\bullet+}$, which arise from oxirene molecules, $[\overline{CH{=}CHO}]$, being unstable on the time and energy scale of these experiments. The presence of a recovery signal at *m/z* 42 in the neutralization–reorientation mass spectra is ascribed to cogeneration of $[CH_2{=}C{=}O]^{\bullet+}$.

Experiments are in progress to identify the analogous species $[\overline{CH{=}CHNH}]^{\bullet+}$, $[\overline{CH{=}CHS}]^{\bullet+}$, and their neutral counterparts.

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Registry No. Oxirene radical cation, 94664-69-4; vinylene carbonate, 872-36-6; oxazole, 288-42-6; isoxazole, 288-14-2; oxirene, 157-18-6; xenon, 740-63-6.

Structure and Energetics of $C_4H_4^{\bullet+}$ in the Gas Phase. Photoelectron Spectrum of Methylenecyclopropene

Stuart W. Staley* and Timothy D. Norden

Contribution from the Departments of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, and University of Nebraska—Lincoln, Lincoln, Nebraska 68588.

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Abstract: The adiabatic and vertical ionization energies of methylenecyclopropene (**1**) have been determined by photoelectron spectroscopy to be 8.15 ± 0.03 and 8.41 ± 0.05 eV, respectively. An analysis of the A_1 vibrational frequency difference ($\Delta\nu$) on going from the ground state to the $^2B_2$ (π) state of the radical cation of **1** ($\mathbf{1}^{\bullet+}$) has led to an explanation for the relatively small value of $\Delta\nu$ obtained on comparing cyclopropenone (**3**) and $\mathbf{3}^{\bullet+}$. The heats of formation ($\Delta H_f{}^\circ{}_0$) of $\mathbf{1}^{\bullet+}$ and cyclobutadiene radical cation are calculated to be 281.5 ± 3 and 293 ± 4 kcal/mol, respectively. Both these values and the *m/z* 26/27 ratios obtained from collisionally activated decomposition spectra of *m/z* 52 ions generated from **1**, benzene, and pyridine support the assignment of $\mathbf{1}^{\bullet+}$ as the lowest energy structure of $C_4H_4^{\bullet+}$ in the gas phase.

The energetics and structures of C_4H_4 radical cations ($C_4H_4^{\bullet+}$) obtained as fragmentation products of larger molecules in the gas phase have attracted considerable interest in recent years. The consensus is that *at least* two different ions are formed, a cyclic species and one or more linear species, which occur in various proportions depending on the conditions and origin. Both the cyclobutadiene radical cation[1] and the methylenecyclopropene radical cation ($\mathbf{1}^{\bullet+}$)[1d,2] have been suggested as structures for the lowest energy form of $C_4H_4^{\bullet+}$, but firm evidence in support of either structure has not been reported. Since the values of the heats of formation ($\Delta H_f{}^\circ{}_0$) of these cations are central to the analysis of this problem, the direct determination of the adiabatic ionization energy (IE_a) of methylenecyclopropene (**1**) is of considerable interest.

From a spectroscopic standpoint, **1** is an interesting molecule for several reasons. Because of its high ring strain, the manifolds of σ and σ^* orbitals are expected to be shifted significantly relative to those of unstrained hydrocarbons. In addition, **1** is an ex-

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(1) (a) Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309. (b) Rosenstock, H. M.; McCulloh, K. E.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 327. (c) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343. (d) Lifshitz, C.; Gibson, D. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 157. (e) Rosenstock, H. M.; Dannacher, J.; Liebman, J. F. *Radiat. Phys. Chem.* **1982**, *20*, 7. (f) Ray, J. C., Jr.; Danis, P. O.; McLafferty, F. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 4408.

(2) (a) Baer, T.; Willett, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076. (b) Ausloos, P. *J. Am. Chem. Soc.* **1981**, *103*, 3931. (c) Wagner-Redeker, W.; Illies, A. J.; Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 5719. (d) van der Hart, W. J. *Org. Mass Spectrom.* **1988**, *23*, 187.

0002-7863/89/1511-0445$01.50/0

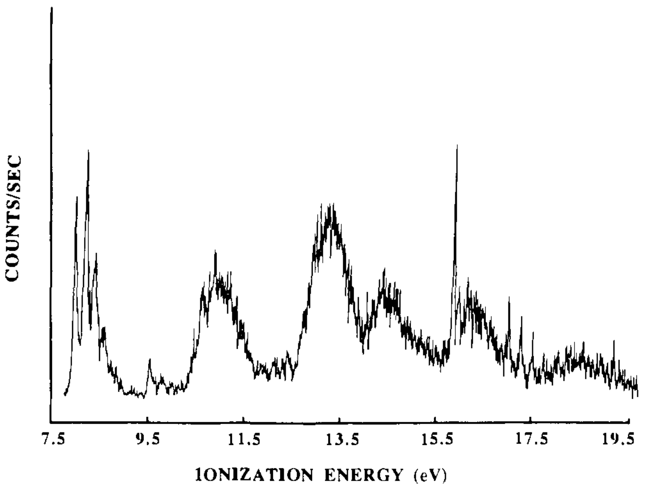

Figure 1. He I photoelectron spectrum of methylenecyclopropene. The sharp peaks between 15.5 and 17.5 eV result from nitrogen.

Table I. Experimental Ionization Energies and Molecular Orbital Energies for Methylenecyclopropene[a]

		HF/6-31G*		MP2/6-31G*	
orbital	exptl IE[b]	calcd	scaled[c]	calcd	scaled[d]
$2b_2$ (π)	8.41[e]	−7.91	−8.54	−7.88	−8.25
$4b_1$ (π')	10.95	−11.80	−11.53	−11.81	−11.31
$1b_2$ (π)	13.1[f]	−13.87	−13.12	−13.66	−12.76
$6a_1$		−14.30	−13.45	−14.14	−13.13
$3b_1$	14.3	−15.69	−14.52	−15.62	−14.29
$5a_1$	15.9	−17.74	−16.09	−17.65	−15.87
$4a_1$	18.1	−20.63	−18.31	−20.50	−18.09

[a] In electronvolts. [b] 0.1 eV unless indicated otherwise. [c] Reference 14. [d] $-\mathrm{IE} = 0.780E_{\mathrm{MO}} - 2.103$. [e] Calculated from the centroid of the first band by the method of ref 15; ±0.05 eV. [f] This peak arises from the overlap of two bands estimated to lie at 12.9 eV ($1b_2$) and 13.3 eV ($6a_1$) (see text).

ceptionally polar molecule, as shown by its gas-phase dipole moment of 1.90 D.[3] It is therefore of interest to examine how the combination of these unusual structural features affects the ionization energies.

Experimental Section

Photoelectron Spectroscopy. Methylenecyclopropene was synthesized in a continuous-flow apparatus[3] by evaporating 150 mg of degassed 2-bromomethylenecyclopropane over 4 h onto a horizontal column filled halfway with potassium *tert*-butoxide on Chromosorb W at a temperature of 115 °C and a pressure of 140 mTorr.[3,4] After passage through the column and two traps maintained at −78 and −90 °C, the effluent gases flowed through the probe of a Perkin-Elmer PS-18 He I photoelectron spectrometer. The probe was connected to a stopcock on the second trap by a glass-to-metal seal and a standard Swagelock fitting. The pressure in the target chamber reached and was maintained at 35 mTorr under the above conditions. The spectrum was calibrated by adding a mixture of argon and xenon to the sample.[5]

Quantum Mechanical Methods. Ab initio molecular orbital calculations were performed with Pople's GAUSSIAN 82 series of programs,[7] which employed the STO-3G[8] and 6-31G*[9] basis sets. Electron correlation effects were incorporated at the MP2/6-31G* level by the use of analytical second-derivative techniques.[10] Molecules were fully optimized at the HF/6-31G* and MP2/6-31G* levels subject only to molecular symmetry constraints. Mulliken overlap populations were calculated for individual orbitals at the STO-3G level by using Gallup's GSCF program and microwave geometries.[11]

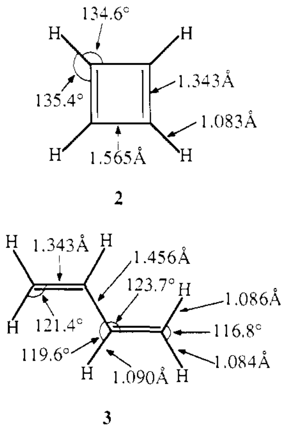

Figure 2. MP2/6-31G* geometry-optimized structures of cyclobutadiene (**2**) and *s-trans*-1,3-butadiene (**3**).

Table II. Calculated and Experimental Energy Data[a]

compd	MP2/6-31G* total energy,[b] hartrees	E_{ZPE},[c] kcal/mol	$\Delta H_f{}^\circ{}_{298} - \Delta H_f{}^\circ{}_0$,[d] kcal/mol	$\Delta H_f{}^\circ{}_{298}$,[e] kcal/mol
methylenecyclopropene	−154.18628[f]	34.8[g]	−1.7	91.9[h,i]
methylenecyclopropane	−155.41602[f]	51.5[j]	−3.7	47.9
cyclopropene	−116.21957[f]	33.8[k]	−2.1	66.2
cyclopropane	−117.46283[f]	49.4[l]	−4.0	12.7
ethylene	−78.29429[m]	30.8[l]	−2.0	12.6
1,3-butadiene	−155.44171[h]	51.4[l]	−3.4	26.3
cyclobutadiene	−154.16484[h,n]	35.3[o]	−2.1	103.8[h,p]
		37.4[q]	−2.9[q]	105.1[h,r]

[a] Related data for some of these compounds can be found in ref 27 and 28. [b] For MP2/6-31G*-optimized geometries. [c] Calculated from the fundamental frequencies (ν_i) in the indicated references; $E_{\mathrm{ZPE}} = {}^1/_2h\sum_i\nu_i$. [d] Calculated by using the equations of ref 27a. [e] Values taken from ref 29 except where indicated otherwise. [f] References 3 and 25. [g] Calculated from the frequencies of ref 20 scaled by 0.85. [h] This work. [i] Previously estimated to be 94 kcal/mol.[30] [j] Reference 31. [k] Reference 21. [l] Reference 32. [m] Reference 33. [n] See also ref 27c and 34, which employed the frozen-core approximation at the MP2/6-31G* level. [o] Reference 27c. [p] Previously calculated to be 103.7 kcal/mol.[27c] [q] Reference 35. [r] Previously estimated to be 105 kcal/mol.[30]

Results

The photoelectron spectrum of **1** (Figure 1) shows six major bands, all of which are attributed to **1** (Table I). The only impurity (or impurities) evident in the spectrum is (are) associated with the weak bands at 9.62 and 9.82 eV. We estimate the purity of **1** to be >95%. Although isobutylene, formed from the decomposition of potassium *tert*-butoxide, was observed in spectra obtained at higher column temperatures (>170 °C), the observed impurities cannot be attributed to this compound since $\mathrm{IE_a}$ and the vertical ionization energy ($\mathrm{IE_v}$) of isobutylene are reported to be 9.23 and 9.45 eV, respectively.[12] The starting material can be eliminated as an impurity since bands that occur at 9.94 and 10.40 eV (1/2 ratio) in the spectrum of 2-bromomethylenecyclopropane[13] are not evident in the spectrum of **1**. The sharp peaks between 15.5 and 17.5 eV in Figure 1 are attributed to nitrogen.

The first band exhibited a vibrational progression with peaks at 8.15, 8.34, 8.53, and 8.70 eV (all ±0.03 eV). The value of $\mathrm{IE_v}$

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(3) Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912.

(4) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699.

(5) Rabalais, J. W. *Principles of Ultraviolet Photoelectron Spectroscopy*; Wiley: New York, 1977; p 43.

(6) These measurements were made in collaboration with Drs. Chhabil Dass and M. L. Gross.

(7) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. *GAUSSIAN 82, Release H*; Carnegie Mellon University: Pittsburgh, PA, 1986.

(8) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(9) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(10) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(11) Gallup, G. A. *Program GSCF*, unpublished. We thank Professor Gallup for the use of this program.

(12) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Halsted: New York, 1981; p 61.

(13) The photoelectron spectrum of 2-bromomethylenecyclopropane displayed bands corresponding to the following IEs and approximate relative areas (eV, relative area): 9.94 (1), 10.4 (2), 11.5 (1), 12.4 (1), 13.1 (1), 14.7 (1), 15.5, 16.2, and 17.6 (1).

(14) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179.

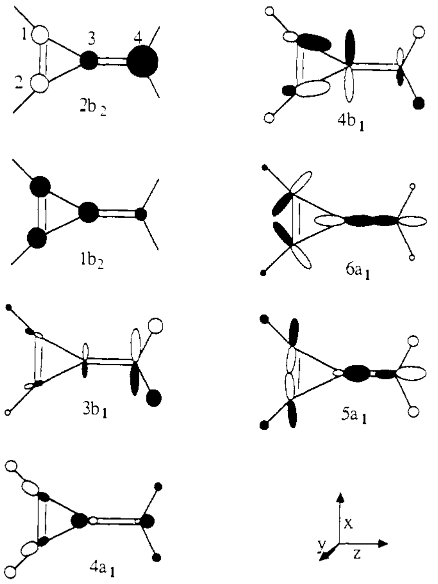

Figure 3. HF/STO-3G orbitals for methylenecyclopropene.

was obtained from the relationship $IE_v = \sigma - \delta$, where σ is the centroid of the vibrational progression and δ is a small correction factor, taken to be 0.03 eV.[15] The intensities of the bands listed in Table I are expected to decrease on going to higher energies, as is generally observed. However, it is evident that the band at 13.1 eV corresponds to two states since the observed intensity is approximately twice that of the 14.3-eV band.

In the course of this study, MP2/6-31*G-optimized structures for D_{2h} cyclobutadiene (**2**) and C_{2h} 1,3-butadiene (**3**) were obtained. Structural parameters for these compounds are given in Figure 2 while total energies are given in Table II.

Discussion

Orbital Assignments. The ionization energies can be related to the negative of the SCF molecular orbital energies on the basis of Koopmans' approximation.[16] The calculated HF/6-31G*//HF/6-31G* and MP2/6-31G*//MP2/6-31G* orbital energies and orbital assignments for **1** are given in Table I along with scaled orbital energies. The corresponding HF/STO-3G wave functions are drawn in Figure 3. IE_v for the first band was calculated from the centroid of the vibrational progression by the method of Smith[15] rather than at the most intense band, as is commonly done, since the former value corresponds better to the calculated orbital energy. IE_a, which corresponds to a transition from the lowest vibrational level of the neutral to the lowest vibrational level of the radical cation, is given by the first band at 8.15 eV. This value was previously estimated to be 7.96 ± 0.1[2b] and 8.28 ± 0.12 eV[1f] from mass spectrometric measurements. IE_v has recently been estimated to be 8.2 eV.[17]

The difference between the energies of the $1b_2$ and $6a_1$ orbitals is ca. 0.4 eV at both scaled computational levels (Table I). This small energy difference, coupled with the relative intensity of the 13.1 eV band, indicates that both orbitals should be assigned to this band. Consequently, the IE_vs corresponding to the $1b_2$ and $6a_1$ orbitals are estimated to be 12.9 and 13.3 eV, respectively.

A plot of the experimental IE_vs versus the MP2/6-31G* orbital energies (Figure 4) yields the equation in Table I with a correlation coefficient of 0.998. The corresponding HF/6-31G* plot gives a similar correlation coefficient (0.999) and slope (0.774). The latter value agrees well with the slope of 0.768 obtained by Wiberg et al. for a variety of other hydrocarbons at the HF/6-31G* level.[14] The linearity of the calculated versus the experimental IE_vs provides strong evidence for the orbital assignments given in Table I.

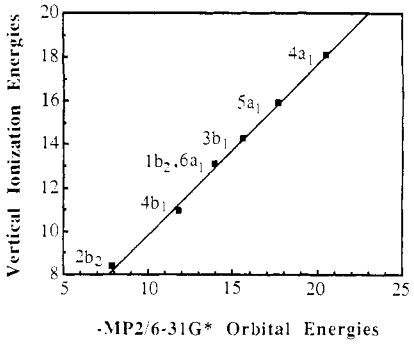

Figure 4. Plot of the negative of the MP2/6-31G* orbital energies against the vertical ionization energies. The average of the $1b_2$ and $6a_1$ orbital energies has been used in this plot.

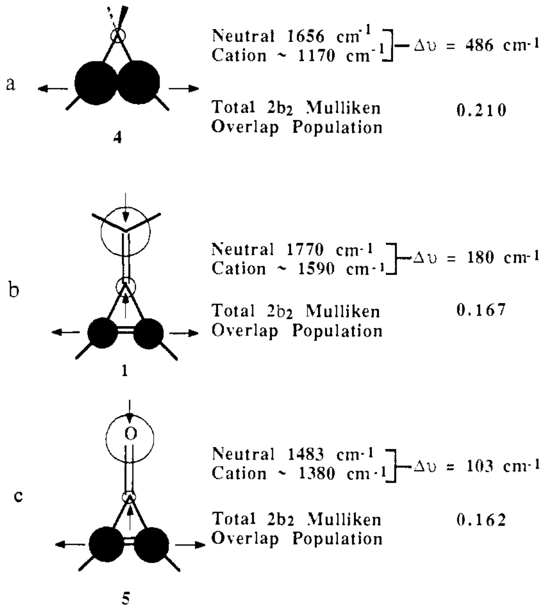

Figure 5. $2b_2$ STO-3G orbitals and total $2b_2$ Mulliken overlap populations for (a) cyclopropene, (b) methylenecyclopropene, and (c) cyclopropenone, along with spectroscopic A_1 vibrational frequencies in the ground and $^2B_2$ radical cation states. The vibrational frequencies for **1**, **4**, $\mathbf{4}^{\bullet+}$, **5**, and $\mathbf{5}^{\bullet+}$ are taken from ref 19, 21–24, respectively, whereas that for $\mathbf{1}^{\bullet+}$ is from this work.

Vibrational Levels. The first band consists of a progression of four peaks at 8.15, 8.34, 8.53, and 8.70 eV, representing formation of the $^2B_2$ radical cation with increasing degrees of vibrational excitation. The peak intervals (1590 (±20), 1520, and 1370 cm^{-1}) show a decrease, owing to positive anharmonicity.[18] Two stretching modes (1770 and 1519 cm^{-1}) have been observed in this region by infrared spectroscopy of **1** isolated in an argon matrix.[19] Both modes are of A_1 symmetry and are therefore possible candidates for excitation in the $^2B_2$ state.[20] However, since the $2b_2$ orbital is a net bonding orbital (the total $^2B_2$ STO-3G Mulliken overlap population is 0.167), the vibrational frequency in the $^2B_2$ cation should be *less* than that in the neutral. This eliminates the 1519-cm^{-1} peak and allows the assignment of the 1590-cm^{-1} progression to the ground-state frequency of 1770 cm^{-1}. The latter corresponds to a symmetrical ring deformation coupled with a C_3C_4 stretch.[20]

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(15) Smith, W. L. *Mol. Phys.* **1973**, *26*, 361.

(16) Koopmans, T. *Physica (Amsterdam)* **1934**, *1*, 104.

(17) Liebman, J. F.; Greenberg, A. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; p 1083.

(18) Reference 5, p 59.

(19) (a) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698. (b) Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1984**, *25*, 5645.

(20) Hess, B. A., Jr.; Michalska, D.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 1449.

(21) Mitchell, R. W.; Dorko, E. A.; Merritt, J. A. *J. Mol. Spectrosc.* **1968**, *26*, 197.

(22) Robin, M. B.; Brundle, C. R.; Kuebler, N. A.; Ellison, G. B.; Wiberg, K. B. *J. Chem. Phys.* **1972**, *57*, 1758.

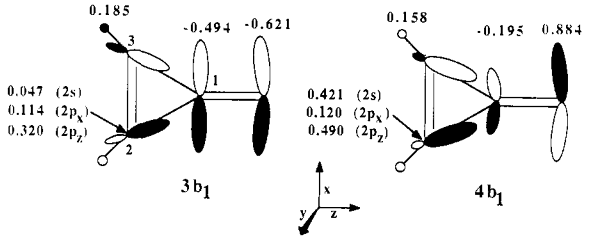


Figure 6. $3b_1$ and $4b_1$ MP2/6-31G* orbitals for cyclopropenone. The effect of the polarization functions at C_1 and O is indicated by the tilting of the orbitals.

The differences between the A_1 vibrational frequencies in the ground and $^2B_2$ cation states ($\Delta\nu$) as well as the total $2b_2$ Mulliken overlap populations are listed in Figure 5 along with drawings of the $2b_2$ orbitals for **1**, cyclopropene (**4**), and cyclopropenone (**5**). All frequencies are for the gas phase except for that of **5**, which was reported for the liquid.[23a] It is interesting to note that $\Delta\nu$ decreases in the same order as the total Mulliken overlap population (**4** > **1** > **5**), as would be expected. Indeed, Harshbarger et al. have previously related the greater value of $\Delta\nu$ in **4** relative to **5** to the greater C=C π Mulliken overlap population in the former compound.[24] About 70–80% of the potential energy of the 1483-cm^{-1} band of **5** is calculated to be in the C=C coordinate.[23b,c] However, the total Mulliken overlap populations for **1** and **5** are almost equal and the ring C=C population for **5** is greater, whereas *the $\Delta\nu$ value for 1 is almost twice as large as that for 5*. How can this be understood?

One possibility, of course, is that the Mulliken overlap populations do not give a very accurate reflection of the bonding in these highly polar and highly strained compounds. However, we believe that, because of the similarity of these compounds, the *differences* in Mulliken overlap population are a reasonable measure of the *relative* changes in π bonding.

A second possibility is that intermolecular interactions between molecules of **5** reduce the vibrational frequency in the liquid state, which would tend to make the $\Delta\nu$ value appear unexpectedly small. This effect undoubtedly plays a role, although we cannot evaluate its magnitude with the available data.

Finally, we suggest that the following effect also plays a role. We have recently proposed that there is substantial interaction of the in-plane (π') lone pair on oxygen (O(2p$_x$)) with the $3b_1$ and $4b_1$ orbitals of the cyclopropene ring (Figure 6).[25] The former (four-electron) interaction causes polarization of the ring orbital away from the carbonyl carbon (C_1) and an increase in the antibonding character at C_2C_3 whereas the latter interaction results in two-electron donation into $4b_1$ of the ring, which is also antibonding at C_2C_3. These π' interactions are reflected by a change in total b_1 (MP2/6-31G*) Mulliken overlap population at C_2C_3 of −0.116 on going from **4** to **5**.

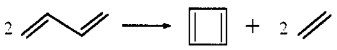
Since about half of the $2b_2$ wave function in **5** is located on oxygen (Figure 5), this atom loses substantial π-electron density and becomes much more electronegative in the $2B_2$ state of $\mathbf{5}^{\bullet+}$. Consequently, both of the above lone pair–ring interactions are reduced, resulting in an *increase* in C_2C_3 π' bonding. This would counteract the reduced π bonding at C_2C_3 that occurs on ionization and provides a reasonable explanation for at least part of the reduction in $\Delta\nu$ for **5** relative to **1**.

Heat of Formation and Structure of $C_4H_4^{\bullet+}$ in the Gas Phase. It is now generally agreed that the majority of C_4H_4 radical cations originating from benzene and pyridine at threshold have cyclic structures.[1,2] The heat of formation ($\Delta H_f{}^\circ{}_0$) of this species has been determined to be in the range of 276–283 kcal/mol.[1a,b,d-f,2a,26] This eliminates the possibility of a linear species since the values of $\Delta H_f{}^\circ{}_{298}$ for the vinylacetylene and butatriene radical cations have been determined to be ca. 290–294 kcal/mol.[1b] However, the problem of which cyclic species, $\mathbf{2}^{\bullet+}$[1] or $\mathbf{1}^{\bullet+}$,[2] is represented by $C_4H_4^{\bullet+}$ has not been resolved. We now present an analysis of this problem employing our value of IE_a for **1** and new computational data.

In Table II we have listed the ab initio total energies, zero-point vibrational energies (E_{ZPE}), heat of formation corrections on going from 0 to 298 K ($\Delta H_f{}^\circ{}_{298} - \Delta H_f{}^\circ{}_0$), and $\Delta H_f{}^\circ{}_{298}$ values for seven hydrocarbons. The values of E_{ZPE} have been calculated from experimental or calculated and scaled vibrational frequencies whereas the standard formulas given by Hehre et al. were employed for the temperature corrections to $\Delta H_f{}^\circ$.[27a] The calculated frequencies of **1** were scaled by a factor of 0.85 because this was the ratio found on comparing four observed frequencies[19] with the corresponding calculated frequencies.[20] If a scaling factor of, e.g., 0.9 were to be more appropriate, then the calculated values of E_{ZPE}, $\Delta H_f{}^\circ{}_0$, and $\Delta H_f{}^\circ{}_{298}$ for **1** would increase by 2.0 kcal/mol.

From the heats of reaction calculated from the data in Table II for homodesmotic reactions 1 and 2, we calculate $\Delta H_f{}^\circ{}_0$ values


(1)


(2)

of 93.6 and 107 kcal/mol for **1** and **2**, respectively. From these values and those of IE_a for **1** and **2** (8.15 and 8.1 eV,[36] respectively), one obtains values of 281.5 ± 3 and 294 ± 1 kcal/mol for $\Delta H_f{}^\circ{}_0$ of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, respectively. The value for $\mathbf{1}^{\bullet+}$ is the only one that is within the experimentally determined range for $C_4H_4^{\bullet+}$ produced at threshold.

Note that we have not considered other C_4H_4 isomers. However, because of their high strain energies[30,37] and lack of conjugation, the heats of formation of their radical cations are expected to be significantly greater than that of $\mathbf{1}^{\bullet+}$.

We also determined the collisionally activated decomposition (CAD) spectrum of $C_4H_4^{\bullet+}$ from **1** (obtained at 8 keV by using helium as the collision gas)[38] to be essentially identical with the

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(23) (a) Brown, F. R.; Finseth, D. H.; Miller, F. A.; Rhee, K. H. *J. Am. Chem. Soc.* **1975**, *97*, 1011. (b) Tuazon, E. C.; Finseth, D. H.; Miller, F. A. *Spectrochim. Acta, Part A* **1975**, *31A*, 1133. (c) Schubert, R.; Ansmann, A.; Bleckmann, P.; Schrader, B. *J. Mol. Struct.* **1975**, *26*, 429.

(24) Harshbarger, W. R.; Kuebler, N. A.; Robin, M. B. *J. Chem. Phys.* **1974**, *60*, 345.

(25) Staley, S. W.; Norden, T. D.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 7641.

(26) (a) Eland, J. H. D.; Berkowitz, J.; Schulte, H.; Frey, R. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 297. (b) Rosenstock, H. M.; Stockbauer, R.; Parr, A. C. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 323. (c) Lifshitz, C. *J. Phys. Chem.* **1982**, *86*, 606. (d) Zang, J. J.; El-Sayed, M. A.; Rebentrost, F. *Chem. Phys.* **1985**, *96*, 1. (e) Silberstein, J.; Salman, I.; Levine, R. D. *J. Phys. Chem.* **1985**, *89*, 5573. (f) Arakawa, R.; Arimura, M.; Yoshikawa, Y. *Int. J. Mass Spectrom. Ion Processes* **1985**, *64*, 227. (g) Arakawa, R.; Yoshikawa, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 49.

(27) (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. (c) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

(28) George, P.; Trachtman, M.; Brett, A. M.; Bock; C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.

(29) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986; p 89.

(30) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617.

(31) Mitchell, R. W.; Merritt, J. A. *Spectrochim. Acta, Part A* **1971**, *27A*, 1609.

(32) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*, NSRDS-NBS 6,11,17; U.S. Department of Commerce, National Bureau of Standards: Washington, DC.

(33) *The Carnegie Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie Mellon University: Pittsburgh, PA, 1983.

(34) Hess, B. A., Jr.; Čársky, P.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 695.

(35) Dorofeeva, O. V.; Gurvich, L. V.; Jorish, V. S. *J. Phys. Chem. Ref. Data* **1986**, *15*, 437.

(36) Kreile, J.; Münzel, N.; Schweig, A.; Specht, H. *Chem. Phys. Lett.* **1986**, *124*, 140.

(37) (a) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292. (b) Fitzgerald, G.; Saxe, P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 690. (c) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 865. (d) Hess, B. A., Jr.; Allen, W. D.; Michalska, D.; Schaad, L. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 1615.

(38) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307.

CAD spectrum of $C_4H_4^{\bullet+}$ generated from benzene and pyridine at threshold. Bowers and co-workers have recently suggested that the *m/z* 26/27 peak ratio can be approximately equated to the ratio of $\mathbf{1}^{\bullet+}$ and vinylacetylene radical cation in the ion beam.[2c,39] Our ratios of 6.2, 4.2, and 4.1 from **1**, benzene, and pyridine, respectively, suggest a preponderance of $\mathbf{1}^{\bullet+}$, although some linear ions may be present in the spectrum of **1**. It is significant that a greater proportion of *m/z* 26 occurs in the latter spectrum, as would be expected if this ion arises from the dissociation of $\mathbf{1}^{\bullet+}$. Interestingly, Tureček et al. have recently reported that a CAD spectrum of C_4H_4 produced by pyrolysis of 2-chloromethylenecyclopropane showed a *m/z* 26/27 peak ratio of 3.2, as compared with a ratio of 4.2 for $C_4H_4^{\bullet+}$ from benzene.[40] These ratios are in accord with their conclusion that vinylacetylene is the major C_4H_4 product of pyrolysis.

In summary, all currently available evidence points to a value of ca. 281 kcal/mol for $\Delta H_f{}^\circ{}_0$ of the lowest energy structure of $C_4H_4^{\bullet+}$. This, along with *m/z* 26/27 ratios from CAD spectra of $C_4H_4^{\bullet+}$ strongly supports the conclusion that the predominant structure of $C_4H_4^{\bullet+}$ *at threshold* is the methylenecyclopropene radical cation ($\mathbf{1}^{\bullet+}$).

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Registry No. 1, 4095-06-1; $\mathbf{1}^{\bullet+}$, 79105-72-9; **2**, 1120-53-2; **3**, 106-99-0; **5**, 2961-80-0; $\mathbf{5}^{\bullet+}$, 100815-68-7; methylenecyclopropane, 6142-73-0; 2-bromomethylenecyclopropane, 90246-24-5.

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(39) See also: Knight, J. S.; Freeman, C. G.; McEwan, M. J.; Anicich, V. G.; Huntress, W. T., Jr. *J. Phys. Chem.* **1987**, *91*, 3898.

(40) Tureček, F.; Hājiček, J.; Maquin, F.; Stahl, D. *New J. Chem.* **1987**, *11*, 793.

Gas-Phase Organometallic Chemistry of Ni^+, $NiCO^+$, $NiPF_3{}^+$, and $NiC_5H_5{}^+$ with Aromatic Compounds

Richard Stepnowski and John Allison*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received May 31, 1988*

Abstract: The gas-phase chemistry of Ni^+ and the monoligated nickel cations $NiCO^+$, $NiPF_3{}^+$, and $NiC_5H_5{}^+$ with a series of aromatic compounds is reported here. The phenyl group is largely unreactive and does not appear to prohibit the metal ion from interacting with other parts of these molecules. For some phenyl compounds, C_6H_5X, no reaction is observed for Ni^+. When Ni^+ does react, products such as $NiC_6H_4{}^+$ and $NiC_5H_5{}^+$ are formed—depending on the chemical composition of the attached functional group (X). Ni^+ reacts with benzyl compounds by insertion into the $C_6H_5CH_2$–X bond, frequently followed by charge transfer to form $C_7H_7{}^+$ as a product. The Ni^+ ion is observed to decarbonylate aromatic carbonyl compounds. When a single ligand is attached to the Ni^+, changes in the chemistry are observed. In many cases, the reactivity decreases as the size of the ligand increases, suggesting the importance of steric interactions even for these monoligated species. There are some exceptions, where $NiC_5H_5{}^+$ is most reactive, even though the cyclopentadienyl ligand is the largest. It is suggested that some charge transfer may occur in $NiC_5H_5{}^+$, resulting in increased positive charge on the metal, leading to increased reactivity.

The gas-phase chemistry of transition-metal ions with organic molecules has been extensively studied in recent years by using ion cyclotron resonance (ICR) and ion beam techniques. The reactions of metal and metal-containing ions have yielded fundamental insights into systems that activate bonds in organic molecules.[1] The organic molecules that have been studied include alkanes and alkenes, as well as a variety of monofunctional compounds such as halogens, alcohols, acids, esters, ketones, ethers, amines, nitro compounds, and nitriles. Some multifunctional compounds have also been studied,[2,3] and in addition, the effect of the basic structural features of linear, branched, and cyclic geometries has been investigated. The major reaction mechanisms have been discussed and reviewed.[1]

For small compounds such as alkyl halides (RX),[4] reaction products appear to be formed via a series of elementary steps. First, a transition-metal ion such as Fe^+ inserts into the C–X bond to yield the intermediate R–Fe^+–X. If the R group is an ethyl group or larger, a β-H shifts to yield a complex of the form $(C_nH_{2n})Fe^+(HX)$. The complex dissociates in a competitive ligand loss step.[3] For more complex functional groups (e.g., carboxylic acids), insertion into bonds within the functional group can also be important.[5,6]

The role of the alkyl group in such reactions has been studied. The extent of branching can affect the overall reactivity. For example, ions such as Co^+ do not appear to insert into the C_3H_7–CN bond in *n*-propyl cyanide, but the insertion does occur for isopropyl cyanide.[7] For straight-chain polar organic compounds, the length of the chain is an important factor in determining the number and types of products. For example, Co^+ reacts with ethanol by inserting into the C–OH bond, which ultimately

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(1) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627.

(2) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 281.

(3) Tsarbopoulos, A.; Allison, J. *Organometallics* **1984**, *3*, 86.

(4) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(5) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 31.

(6) Cassidy, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 6125.

(7) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

0002-7863/89/1511-0449$01.50/0